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微米铁复合生物碳源对地下水中1,2-二氯乙烷的高效去除

吴乃瑾, 宋云*, 魏文侠, 王海见, 孙仲平

(轻工业环境保护研究所, 工业场地污染与修复北京市重点实验室, 北京 100089)

摘要: 1,2-二氯乙烷(1,2-DCA)是一类地下水中常见的难降解饱和氯代烃,为探究厌氧条件下零价铁(ZVI)协同生物作用对其降解规律,采集北京市某氯代烃污染场地地下水及含水层土壤,利用微宇宙实验体系,通过添加由微米级零价铁(mZVI)、生物碳源及营养组成的复合药剂,考察不同条件下1,2-DCA的去除效果,并对地下水理化参数的变化进行长期监测.结果表明:复合药剂添加量为3%时,恒温、避光、匀速振荡的反应条件下,15 d内地下水中的1,2-DCA即可降至低于检出限.中性pH及 SO_4^{2-} 的存在更有利于1,2-DCA的脱氯降解.30 d后仅检测到体系中明显的乙烯产生,推测双脱氯消除为1,2-DCA在该体系内的主要降解途径.此外,复合药剂加入后,地下水可长时间维持较低的氧化还原电位(-100 ~ -300 mV)、溶解氧($<0.5 \text{ mg}\cdot\text{L}^{-1}$)以及适宜的pH值(6.5 ~ 7.5),利于厌氧微生物活性的维持及脱氯反应的进行.

关键词: 氯代烃; 1,2-二氯乙烷(1,2-DCA); 地下水; 微米零价铁(mZVI); 生物碳源

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High Efficiency Removal of 1, 2-Dichloroethane from Groundwater by Microscale Zero-valent Iron Combined with Biological Carbon Source

WU Nai-jin, SONG Yun*, WEI Wen-xia, WANG Hai-jian, SUN Zhong-ping

(Beijing Key Laboratory of Industrial Land Contamination and Remediation, Environmental Protection Research Institute of Light Industry, Beijing 100089, China)

Abstract: In order to explore the degradation mechanism of 1,2-dichloroethane (1,2-DCA), which is one of the refractory saturated chlorinated hydrocarbons, the groundwater and aquifer soil from a chlorinated hydrocarbon contaminated site in Beijing were collected to carry out microcosm experiments under anaerobic conditions using zero-valent iron (ZVI) coupled with biological action. The removal rate of 1,2-DCA under different conditions was investigated by adding a composite agent consisting of micron zero-valent iron (mZVI), a biological carbon source, and a few nutrients. Changes of the groundwater physical and chemical parameters were monitored. The results showed that, when the dosage of the composite agent reached 3%, the concentration of 1,2-dichloroethane could be reduced to below the detection limit within 15 days. Neutral pH and the presence of SO_4^{2-} were more conducive to the dechlorination of 1,2-DCA. After 30 days, an obvious increase in the ethene concentration was detected ($0.17\text{--}0.52 \text{ mg}\cdot\text{L}^{-1}$) and no significant vinyl chloride, chloroethane, or ethane was observed in the microcosms, illustrating that the dihaloelimination was the main degradation pathway of 1,2-DCA in the system. In addition, the groundwater could maintain a low oxidation-reduction potential (-100 to -300 mV), dissolved oxygen ($<0.5 \text{ mg}\cdot\text{L}^{-1}$), and a suitable pH value (6.5-7.5) for a long time under the synergy of mZVI and a biological carbon source. This was beneficial to the activity of anaerobic microorganisms and to the dechlorination reaction.

Key words: chlorinated hydrocarbon; 1,2-dichloroethane (1,2-DCA); groundwater; micron zero valent iron (mZVI); biological carbon source

氯代烃是地下水最为常见的有机污染物之一,多数难降解且具有致癌、致畸、致突变效应.不同于国外,我国当今地下水中高频检出且超标的饱和氯代烃占有较大比重,严重影响了污染区的生活质量^[1~3].近年来,将ZVI用于环境污染治理逐步发展为一种新型、高效的修复手段^[4~7].已报道的各类ZVI修复材料对三氯乙烯、四氯乙烯、三氯乙烷等均显示出较高的活性^[8~10],但是对1,2-DCA的去除率仍较低,即便利用高活性的纳米铁或其它零价金属效果也并不显著^[11,12].Liu等^[13]通过电解还原发现在小分子氯代烃中,1,2-DCA的C—Cl键解离能最

大,脱氯反应所需的活化能最高.因此,单纯利用ZVI不足以快速克服其较高的C—Cl键能.然而场地实验表明,ZVI原位注入含水层后可进一步刺激氯代烃的厌氧生物降解^[14].Zemb等^[15]将mZVI应用到PRB技术修复污染场地时,反而监测到1,2-DCA一定程度的去除,原因是ZVI腐蚀反应生成 OH^- ,中和了含水层酸性物质,为微生物生长提供了中性环境.ZVI还可使地下水

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作者简介: 吴乃瑾(1989~),女,博士,主要研究方向为污染场地修复技术及地下水污染控制, E-mail: wujin310@126.com

* 通信作者, E-mail: liepi_song@163.com

快速达到理想的厌氧环境,产生的 H_2 亦可作为电子供体促进厌氧微生物的生长。

基于此,ZVI 协同生物降解成为氯代烃污染地下水原位修复的研究热点^[16,17]。然而实际含水层中,往往缺乏能源及营养物质,导致 ZVI 后期对微生物的刺激作用缓慢且有限^[18],外加碳源/电子供体则是常用来强化生物作用的方式。工程应用中,mZVI 寿命相对更长,且成本低、生物毒性小,利用 mZVI 协同生物强化对含水层 1,2-DCA 的降解规律仍缺乏相关研究。实验采集北京市某氯代烃污染场地地下水建立微宇宙体系,通过混入有机碳源强化生物作用与 mZVI 协同,考察不同条件下 1,2-DCA

的降解规律及地下水参数变化,同时结合代谢产物分析 1,2-DCA 的主要降解途径,以期为原位修复药剂的工程化应用提供理论支撑。

1 材料与方法

1.1 样品采集

所用地下水及含水层土壤均采自北京市某废弃化工厂氯代烃污染区的第一含水层,该层为相对强透水层,土质为细砂和中砂,取样深度位于 -15 ~ -17 m 处。地下水样经氮气吹脱除去残余的微量氯代烃后冷藏备用,土壤颗粒过 2 mm 筛后备用。地下水的基本理化参数如表 1 所示。

表 1 实验所用地下水的基本理化参数

Table 1 Basic physicochemical parameters of groundwater for the experiment

| 项目 | TOC /mg·L ⁻¹ | 总铁 /mg·L ⁻¹ | SO ₄ ²⁻ /mg·L ⁻¹ | NO ₂ ⁻ /mg·L ⁻¹ | NO ₃ ⁻ /mg·L ⁻¹ | Cl ⁻ /mg·L ⁻¹ | 硫化物 /mg·L ⁻¹ | 含水层土壤 TOC /mg·L ⁻¹ |
|-----|----------------------------|---------------------------|--|---|---|--|----------------------------|----------------------------------|
| 参数值 | 2.5 | <0.1 | 191 | 0.29 | 12.8 | 189 | <0.05 | <1 |

1.2 实验试剂

为降低药剂成本同时保持高活性,实验选用 200 目的二次还原铁粉(纯度 99.9%)。生物碳源及营养物质(醋酸钠、乳酸钠、乳酸、酵母浸粉、硫酸二氢钾)均为分析纯,乳化油为市售的大豆油与 Toween-80 经高速搅拌制得。1,2-DCA 标准液为中国计量科学研究院生产。

1.3 微宇宙实验的建立

取 50 mL 地下水和 10 g 过筛后的含水层土壤置于 100 mL 血清瓶,模拟实际场地含水层生态条件,建立微宇宙实验体系(microcosm)^[19]。将所需实验材料及试剂共同置于手套箱中,抽真空-充氮气往复 3 次以上,确保微宇宙反应体系的无氧环境。在氮气保护下将各物料按比例加入,用带有特氟龙衬垫的铝盖压紧密封。最后抽取微量 1,2-DCA-甲醇饱和溶液迅速加入血清瓶中,配制 1,2-

DCA 浓度约为 10 mg·L⁻¹ 的反应体系,并用封口膜双重密封。为缩短反应周期,将血清瓶置于恒温(25℃)摇床中避光充分混合反应。结合前期研究基础,在 1 g·L⁻¹ 添加量的基础上考察 4 种生物碳源对 1,2-DCA 降解效果的影响,分别为:SAP(添加醋酸钠);SLP(添加乳酸钠);HAP(添加乳酸);EOP(添加乳化油)。每个实验组均额外加入微量营养组分:0.05 g·L⁻¹ 酵母浸粉,0.005 g·L⁻¹ 磷酸二氢钾。

将筛选出的生物碳源与 mZVI、微量营养在分散剂的辅助下进行复配,制得 mZVI-生物碳源复合药剂。浆液中各组分的质量分数如下:mZVI 为 10%,生物碳源及微量营养为 2%,羧甲基纤维素为 0.4%。设置不同的实验条件,在微宇宙体系中对对比考察复合药剂对 1,2-DCA 的降解效果。本实验设置见表 2。

表 2 不同处理条件下 1,2-DCA 降解效果考察实验组设置

Table 2 Experimental design of 1,2-DCA degradation under different treatment conditions

| 实验组 | 地下水/mL | 含水层土壤/g | 超纯水/mL | 1,2-DCA/mg·L ⁻¹ | 处理方式及添加组分 |
|---------|--------|---------|--------|----------------------------|--|
| BLK(空白) | — | — | 50 | 10 | — |
| 灭菌组 | 50 | 10 | — | 10 | 121℃ 灭菌 6 次(1~2 h/次) |
| 自然组 | 50 | 10 | — | 10 | — |
| mZVI | 50 | 10 | — | 10 | mZVI(200 目) |
| 复合药剂组 | 50 | 10 | — | 10 | 不同添加量、不同 pH、外加 NO ₃ ⁻ 、SO ₄ ²⁻ |

1.4 复合药剂对地下水环境的影响

为确定 mZVI 的加入与是否能够作为脱氯反应提供更有利的水体环境,利用新鲜采集的地下水样品,设置两个实验组(添加复合药剂、仅添加生物

碳源及微量营养组成的复合药剂)于暗处静置,分别记为实验组 1 和实验组 2,每组设置 3 种不同的添加量(质量分数分别为 1%、3%、5%),间隔一定的时间抽取水样监测参数变化:pH 值、氧化还原

电位(ORP)、溶解氧(DO)。

1.5 污染物及代谢产物浓度检测

参考文献[20]的方法,间隔一定时间,将摇床中的反应瓶静置12 h以上,确保各相平衡后,抽取0.42 mL液体检测1,2-DCA的浓度,抽取1 mL气体监测其中乙烯、乙烷、氯乙烯、氯乙烷的浓度变化。吹扫捕集进样-气相色谱-质谱联用(型号:安捷伦7890B-5977A)用于测定1,2-DCA浓度,选用安捷伦DB-624型色谱柱(60 m × 250 μm × 1.4 μm),检测器温度260℃、保留时间19 min、分流比20:1。气相色谱(型号:安捷伦7890B)用于测定气相中的产物浓度,选用安捷伦HP-PLOT/Q型色谱柱(30 m × 320 μm × 20 μm),前进样口温度220℃、分流比20:1、FID检测器温度200℃、保留时间15 min、尾气吹扫流量30 mL·min⁻¹。利用SG-98型多参数水质测定仪监测地下水理化参数的变化,利用Thermo Fisher ICS-600离子色谱仪分析硫酸根浓度变化。

2 结果与讨论

2.1 最适碳源的筛选

厌氧条件下补充碳源、电子供体可加速生物降解,可溶性及缓释碳源在不同的野外研究中得到了广泛应用^[21]。本实验选取醋酸钠、乳酸钠、乳酸、乳化油这4种碳源,分别考察了微宇宙体系下1,2-DCA的去除效果(如图1)。30 d内实验组SAP、SLP中污染物的降解量均可达90%,SAP组前期对1,2-DCA的去除速率略高于SLP组。HAP组30 d内对1,2-DCA去除率则相对较低,约为60.5%。有研究表明,厌氧条件下发生还原脱氯反应的最佳pH值在6.8~7.5之间^[22],该范围最有利于厌氧菌生命活动的进行,因此保持含水层适宜的pH值尤为重要,而HAP中乳酸的添加导致体系pH值显著降低,超出微生物的最佳生长范围,从而在后期抑制了厌氧微生物的生命活动。添加乳化油的EOP组,1,2-DCA浓度先在短期内出现了明显的降低而后恢复到初始值,继而缓慢降低,由此推测乳化油的添加前期对1,2-DCA以溶解、吸附作用为主,后随反应时间的延长而释放导致浓度反弹。同时由于乳化油为长链大分子碳源,微生物需一定的时间先将其分解为小分子脂肪酸才能进一步利用。对比以上结果,决定复合药剂中选择醋酸钠为最适碳源,同时添加微量酵母浸粉及磷酸盐保证厌氧菌的快速生长。此外醋酸钠在自然状态下为固体粉末,与mZVI可在干物质状态下进行预混,利于复合药剂的制备及运输。

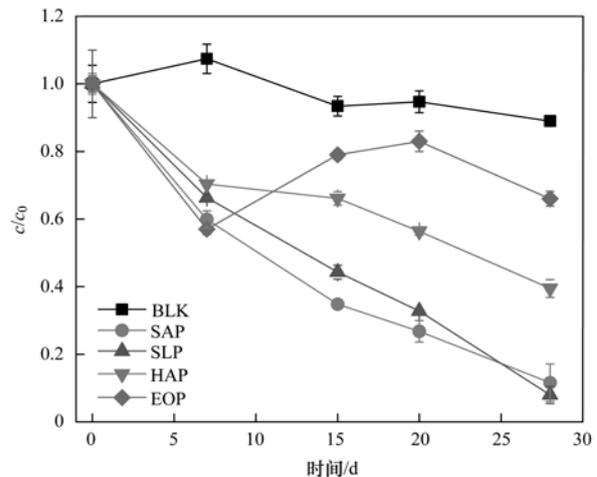


图1 添加不同生物碳源对1,2-DCA去除率的影响

Fig. 1 Effect of different biological carbon sources on the 1,2-DCA removal rate

2.2 不同处理条件下1,2-DCA降解效果的对比

图2为不同处理方式及不同复合药剂添加量下,地下水中1,2-DCA的去除效果。从中看出,空白对照组和灭菌组30 d内1,2-DCA浓度没有发生显著变化,因此含水层土壤的吸附及氯代烃在该处理方式下的挥发可忽略不计。自然组中1,2-DCA的降解趋势非常缓慢。仅添加mZVI的实验组15 d后1,2-DCA浓度出现了小幅降低,表明初期mZVI对其还原作用较弱,后期可能由于ZVI腐蚀反应对体系环境的改变,一定程度上刺激了生物降解。而添加mZVI-生物碳源复合药剂的各实验组,1,2-DCA的去除率显著加快。药剂添加量为1%时,30 d后对1,2-DCA的降解效果可达66.3%,当添加量增至2%和3%时,1,2-DCA浓度分别在30 d内和15 d内即可低于检出限。结合图1的降解曲线,说明在该反应体系中mZVI与生物碳源强化的双重刺激

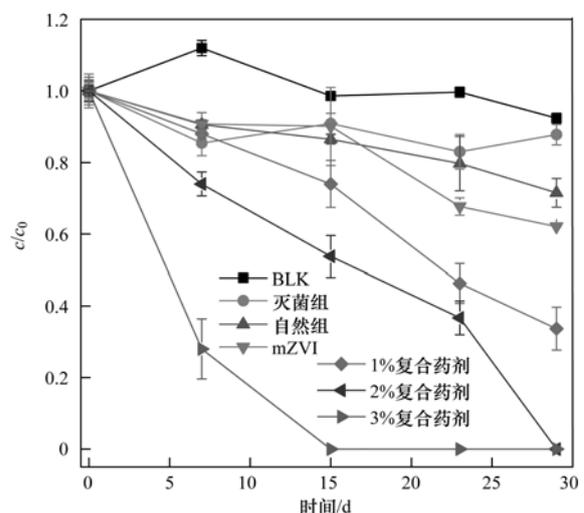


图2 不同处理条件下1,2-DCA浓度的变化

Fig. 2 Variation of 1,2-DCA concentration under different treatment conditions

可明显加速 1,2-DCA 在厌氧条件下的降解效率。

2.3 pH 值对复合药剂去除 1,2-DCA 的影响

地下水的酸碱性是影响 mZVI 活性及厌氧微生物生命活动的关键因素^[23], 本实验利用 $0.5 \text{ mol}\cdot\text{L}^{-1}$ 的盐酸和氢氧化钠调节 pH, 考察了复合药剂添加量为 2% 时, 不同 pH 值对 1,2-DCA 去除率的影响(图 3)。自然条件下加入药剂后地下水 pH 值约为 7.58。从图中看出, 酸性条件下, 1,2-DCA 初期降解速度较快, 这是由于 H^+ 可腐蚀 mZVI 颗粒表面的钝化层, 释放活性位点, 加速反应进行, 同时腐蚀反应产生大量 H_2 , 为微生物提供充足的电子供体。然而随着 mZVI 的快速消耗反而导致 1,2-DCA 的降解速率在 15 d 以后明显变缓, 并且 Fe^{2+} 水解造成体系进一步酸化, 抑制了生物作用的发挥, 最终去除率低于 60%。而碱性条件下, 由于过量 OH^- 的存在, mZVI 表面更易形成钝化层, 加上该条件已超出适宜厌氧微生物生长的最佳范围, 削弱了 mZVI 与生物作用的协同性, 因此降解速率较另外两组都更为缓慢。

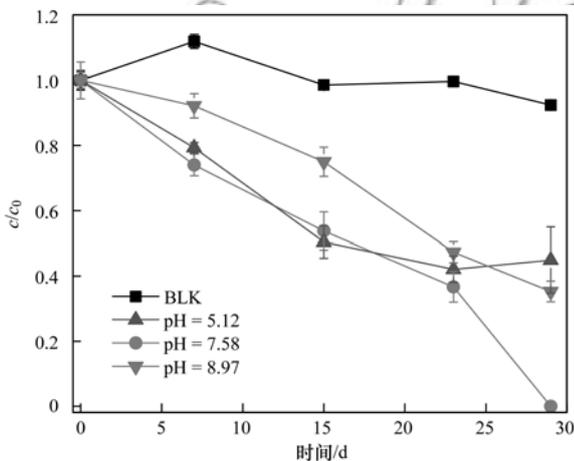


图 3 不同 pH 值对 1,2-DCA 降解率的影响

Fig. 3 Effects of different pH values on the degradation rate of 1,2-DCA

2.4 阴离子对复合药剂去除 1,2-DCA 的影响

电子受体常常是厌氧生物群落组成的限制资源, 也是决定厌氧物种组成的主要因素, 因此地下水中可作为微生物电子受体的阴离子(如 SO_4^{2-} 、 NO_3^-)也会影响同样作为电子受体的 1,2-DCA 的降解效率。实验分别在微宇宙体系中额外添加了 $200 \text{ mg}\cdot\text{L}^{-1}$ 的 SO_4^{2-} 和 NO_3^- , 考察该条件下 1,2-DCA 浓度变化趋势(图 4), 复合药剂的添加量均为 2%。额外添加 SO_4^{2-} 的实验组 10 d 后 1,2-DCA 的降解出现了明显的加速过程, NO_3^- 的加入则明显抑制了 1,2-DCA 的降解, 说明 NO_3^- 与 1,2-DCA 更多地是产生竞争作用, 从而降低了反应速率。此外, NO_3^-

的加入会额外消耗 mZVI 及生物碳源, 多方面阻碍 1,2-DCA 的降解路径。而 SO_4^{2-} 更倾向于在适宜的 ORP 下通过生物作用被还原, 已证实参与到该过程中的脱硫杆菌等厌氧/兼氧微生物可同时代谢天然底物和氯化有机物^[19,24], 因此推测体系中 1,2-DCA 的降解可能与 SO_4^{2-} 生物还原过程密切相关。参与该过程的硫酸盐还原菌(SRB)属于异养菌, 足够的碳源可为其生长提供能源和电子供体, 有机碳源的类型对维持 SRB 的活性及稳定性十分重要^[25]。实验进一步对反应体系中 SO_4^{2-} 浓度的变化进行了检测, 从图 5 看出, 加入复合药剂的地下水 SO_4^{2-} 大量消耗, 随 SO_4^{2-} 浓度的升高消耗量也相对增加, 说明 mZVI 和醋酸钠的共同添加明显刺激了该类菌的生长。结合图 4 中的降解曲线推测 1,2-DCA 的脱氯降解与 SO_4^{2-} 还原过程呈正相关。

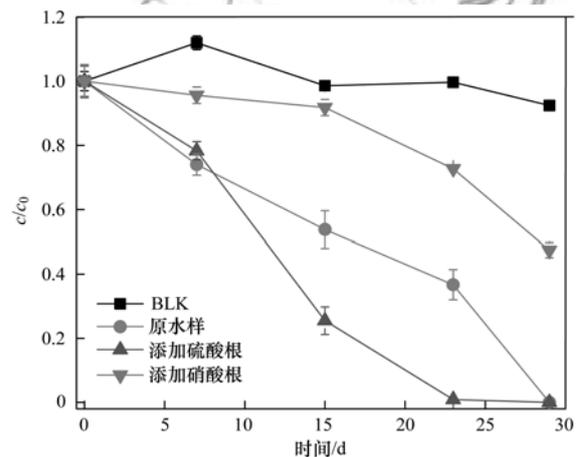


图 4 不同阴离子对 1,2-DCA 降解率的影响

Fig. 4 Effects of different anions on the degradation rate of 1,2-DCA

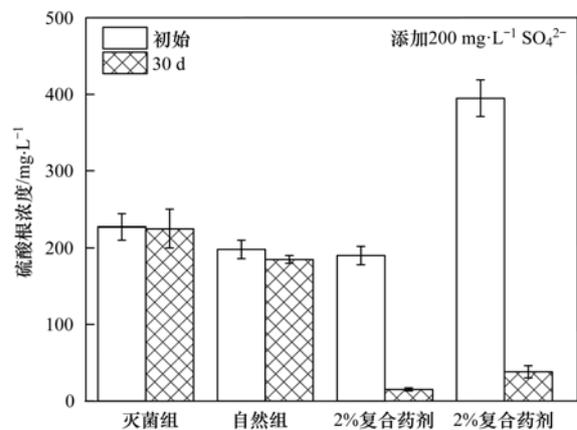


图 5 不同条件下硫酸根浓度变化

Fig. 5 Variation of SO_4^{2-} concentration under different conditions

然而上述过程会导致 H_2S 的不断释放形成毒性累积, 抑制厌氧微生物活性, 并产生恶臭问题^[26]。Wang 等^[27]发现在 1,2-DCA 生物降解过程中加入铁基材料, 可以去除水中 94% 的硫化物, 金

属硫化物的形成降低了 H_2S 浓度以及随后产生的气味问题. 与加药前浅褐色的含水层土壤相比, 复合药剂加入 30 d 后, 可以明显观测到大量的黑色固体颗粒生成(如图 6), 推测生成的黑色沉淀为 SO_4^{2-} 还原过程产生的硫化物与 mZVI 反应生成的 FeS 颗粒, 该过程可能涉及到的反应如反应式(1)~(4)所示, 这说明 mZVI 的加入同样可以有效抑制毒性硫化物的累积, 形成更有利于脱氯反应的环境. 除此之外, 最新研究还表明^[28], 对 ZVI 表面进行硫化改性, 产生的 FeS 保护层还可减缓 ZVI 表面氧化, 加速有机物非生物降解过程中的电子传递.

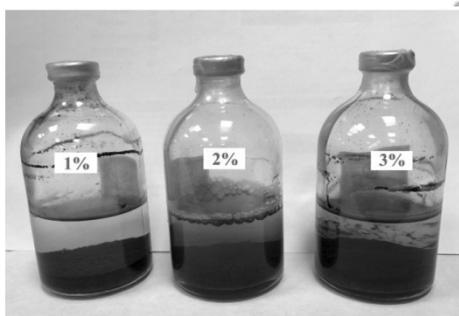
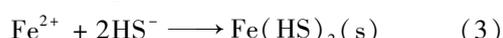
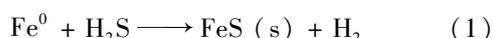


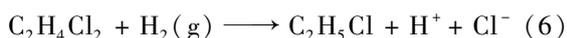
图 6 不同复合药剂添加量的微宇宙体系(30 d 后)

Fig. 6 Picture of the microcosm study with different dosage of compound agent (after 30 days)

2.5 代谢产物分析

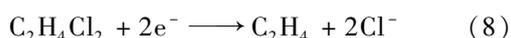
据报道, 厌氧条件下, 1,2-DCA 有可能通过两种途径发生脱氯反应: 氢解反应和 β -消除反应.

氢解反应过程中, 1,2-DCA 会逐级脱去氯原子, 生成氯乙烷及最终产物乙烷, 该反应涉及到的方程式如下^[29]:



反应式(6)一般需在催化剂的存在下才可进行, 如铁的氧化物 Fe_3O_4 .

β -消除反应包括两种途径: ①脱去相邻碳原子上的一个氯原子和一个氢原子生成氯乙烯[反应式(7)]; ②同时脱去相邻碳原子上的两个氯原子, 直接生成乙烯[反应式(8)]:



厌氧条件下, 1,2-DCA 可作为多种微生物的终端电子受体, 其中经二氯消除直接生成乙烯是 1,2-DCA 生物降解的主导机制, 该过程可由脱卤拟球

菌、脱卤杆菌、脱硫杆菌等多种微生物介导, 氯乙烯也可作为生物降解的次要产物少量存在于含水层中^[30]; 1,2-DCA 还可经水解、氢解等非生物过程分解为氯乙烯、醇类、 CO_2 等^[31]. 为了进一步确定该体系中 1,2-DCA 的降解路径, 对加药前后体系中的气体进行了分析, 结果检测到明显的乙烯产生(如图 7), 且随复合药剂添加量的升高而增加($0.17 \sim 0.52 \text{ mg}\cdot\text{L}^{-1}$). 此外, 还检测到极微量的氯乙烯($<0.001 \text{ mg}\cdot\text{L}^{-1}$), 乙烷和氯乙烷则未检出, 说明该体系下 1,2-DCA 发生了生物降解, 实现了彻底脱氯, 且二氯消除是生物降解的主要途径. 微量氯乙烯的出现也表明 1,2-DCA 发生了一定程度的氢解脱氯, 只不过作为次要产物其产量很少. 地下水中 1,2-DCA 初始浓度为 $10 \text{ mg}\cdot\text{L}^{-1}$, 由此推算完全脱氯生成乙烯的理论值约为 $2 \sim 3 \text{ mg}\cdot\text{L}^{-1}$, 而气相中乙烯的浓度较理论值偏低, 这一方面由于液相中的乙烯浓度未检测, 另一方面则有可能是乙烯进一步被微生物利用所致.

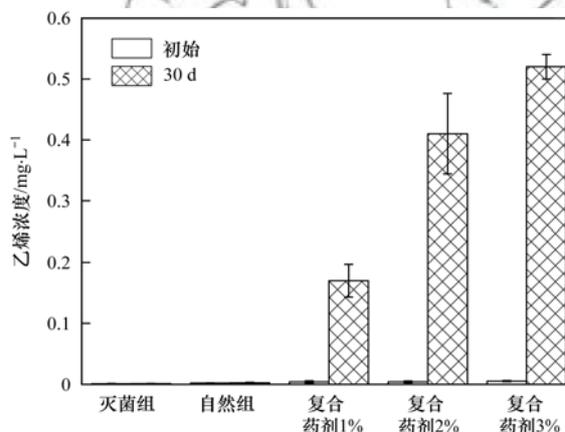


图 7 不同实验条件下各体系乙烯浓度的变化

Fig. 7 Changes of ethylene concentration under different experimental conditions

2.6 复合药剂对地下水环境的影响

图 8 为两个实验组(添加复合药剂-实验组 1; 仅添加生物碳源和营养-实验组 2)中地下水各项理化参数的变化. 复合药剂的添加可使地下水在 6 个月内更加稳定地维持较低的氧化还原电位($-100 \sim -300 \text{ mV}$). 而实验组 2 随药剂增加, pH 值逐步降低至 6 以下, 这归因于碳源被生物降解以后会产生酸性物质而导致地下水酸化. 相较而言, 实验组 1 在添加量为 5% 时, pH 值仍旧维持在 $6.5 \sim 7.5$ 之间, 这正是由于 Fe^0 的腐蚀反应产生 OH^- , 中和了体系产生的酸性物质, 从而对 pH 值起到了明显的缓冲作用. 两组体系的溶解氧变化进一步反映了 mZVI 的加入可长时间使体系维持理想的厌氧环境($\text{DO} < 0.5 \text{ mg}\cdot\text{L}^{-1}$), 利于厌氧微生物的代谢

活动. 综合这 3 种参数的变化规律得出, 该体系下复合药剂的添加量为 3% 时对水环境参数的影响最优, 结合前期 1,2-DCA 的降解效果, 证明该条件下

mZVI 可最大化发挥与厌氧生物作用的协同性, 相关数据为后续中试研究中实验药剂最适添加量提供了依据.

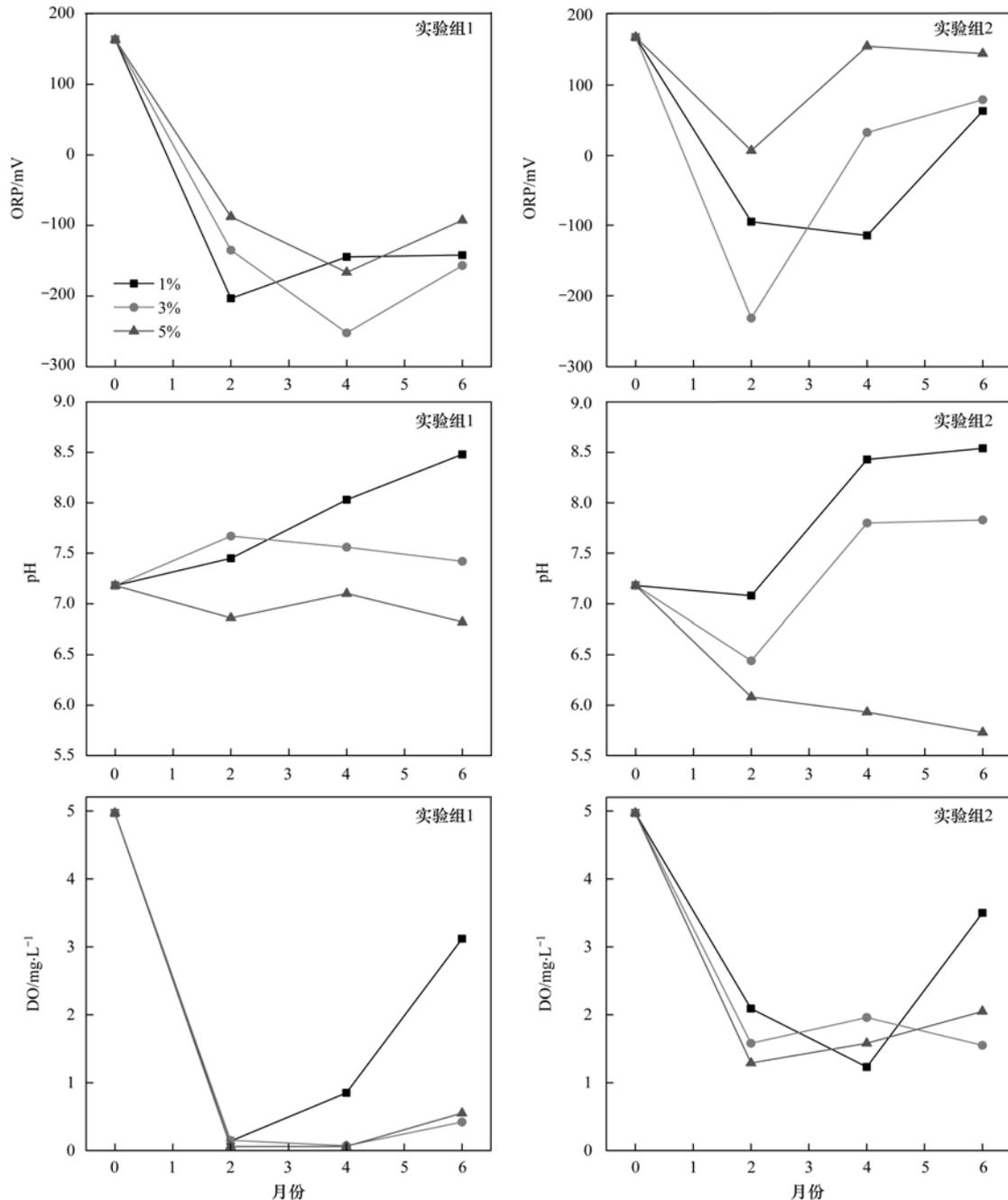


图 8 地下水理化参数 (ORP、pH、DO) 随时间的变化

Fig. 8 Physicochemical parameter (ORP, pH, DO) variations of groundwater over time in two groups

3 结论

(1) mZVI 与生物碳源及营养的共同添加可对地下水中 1,2-DCA 的降解起到明显的协同增效作用. 复合药剂添加量为 3% 时, 1,2-DCA 可在 15 d 内实现完全去除, 中性 pH 和 SO_4^{2-} 的存在更有利于 1,2-DCA 的脱氯降解.

(2) 30 d 后, 气相中明显检测到乙烯生成

($0.17 \sim 0.52 \text{ mg} \cdot \text{L}^{-1}$), 仅检测到微量的氯乙烯 ($< 0.001 \text{ mg} \cdot \text{L}^{-1}$), 未检出乙烷和氯乙烷, 说明经生物作用发生二氯消除是 1,2-DCA 降解的主要途径, 并不会引起有毒副产物的累积.

(3) mZVI 可防止碳源在生物利用过程中导致的地下水酸化, 并消除由硫化物累积而产生的负面影响, 保证地下水长时间维持较低的氧化还原电位 ($-100 \sim -300 \text{ mV}$)、良好的厌氧环境 ($\text{DO} < 0.5$

$\text{mg}\cdot\text{L}^{-1}$)以及适宜的 pH 值(6.5 ~ 7.5), 利于维持厌氧微生物活性及脱氯反应的进行。

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